Causes of deviation from ideal behaviour.Equation of states for real gases; van der Waals equation of state, its derivation and application in explaining real gas behaviour, van der Waals equation expressed in virial form and calculation of Boyle temperature.

Content Type	Notes
Status	Done
Chapter	Gaseous State
Course	Graduation
Reference	Physics walla, uou.ac.in
Subject	Physical Chemistry
Topic	Boyle's Temperature, Deviation, Ideal Gas, Real Gases, Van der Waal, Van der Waals equation
Ruhul Amin	@February 5, 2023 4:52 PM
# Progress (%)	100
Difficulty	Medium

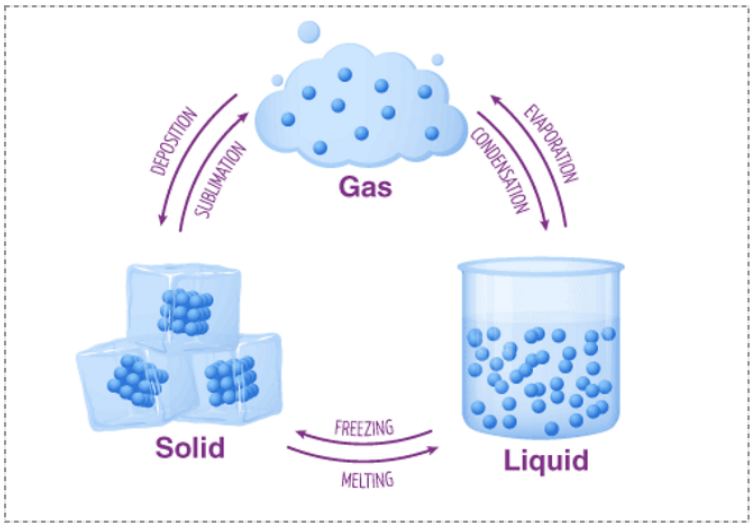
Level	
Mistake type	
Previous Year Questions	

Deviation from ideal behaviour

Cause of deviation from ideal behavior of gas: Because of two important assumptions in Ideal gas:

- **Assuption**: Molecular Volume is negligible as compared to total volume of gas.
- **Reality**: Molecular volume is quite measurable and can not be ignored of gases
- **Assumption**: Gaseous Molecules have no force of attraction in between.
- **Reality** : Gaseous molecules have force of attraction between them.

Evidence of Molecular volume of gas



• Gases can be liquified and solidified in low temperature and High pressure.
• The gas liquified or solidified have some volume.
• This volume of gas is same irrespective of any state.
• liquified and solidified state of gases have force of attraction between molecule
• Solidified gases can be compressed up to certain extend only. Thus gases have

appreciable volume, which is of same order as that occupies by same number of molecules in the solid state

Correction in Volume of Ideal gas for the real gas

Volume of the gas in the available space for the movement of gas molecules. Volume V of an ideal gas is the same as the volume of the container. The dot molecule of ideal gas has zero-volume and the entire space in the container is available for their movement. But von der Waals assume that molecules of real gas are rigid spherical particles which posses a definite volume. The volume of real gas is, therefore ideal volume minus the volume occupied by gas molecules (Fig 2.6). If b is the effective volume of molecules per mole of the gas then corrected volume should be V-b = **V**ideal For n moles **V**ideal = V-nb b is also known as excluded volume.

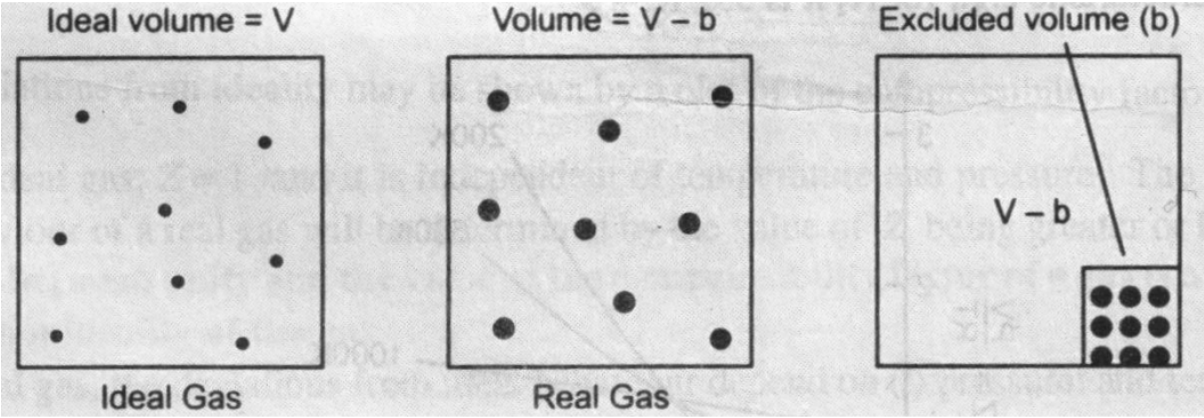


Fig 2.6

Finding value of b

Now let us consider two molecules of radius r colliding with each other (Fig 2.7). Obviously they cannot approach each other closer than a excluded volume.

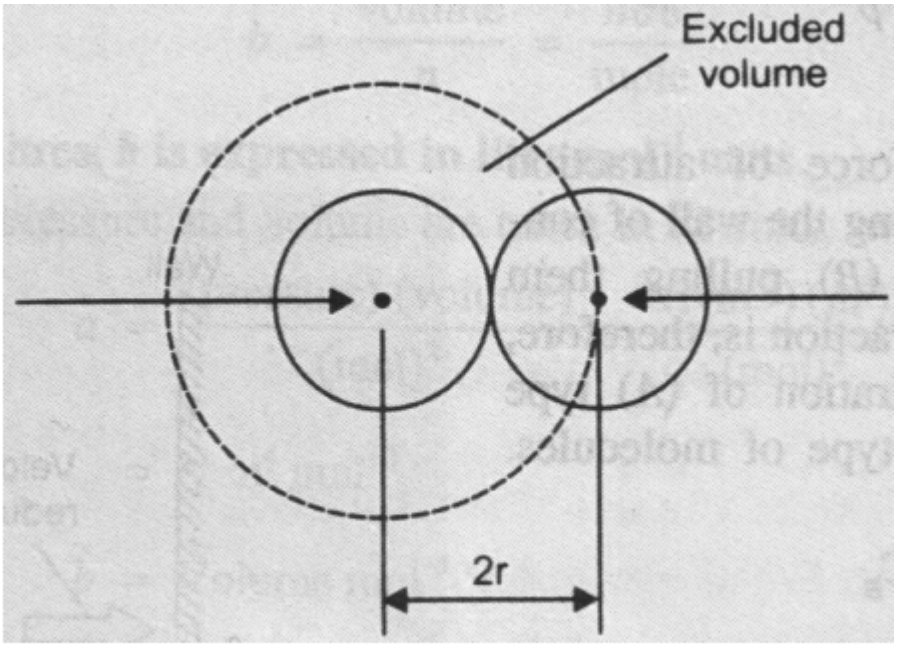


Fig 2.7

Therefore, the space indicated by the dotted sphere having radius 2r will not be available to all other molecules of the gas. In other words the dotted space is excluded volume per pair of molecules. Thus,

Excluded volume for two molecules $= 4/3\ \pi(2r)^3$

$= 8x4/3\pi r^3$

Excluded volume per molecule $= ½\ 8x4/3\pi r^3$

$= 4x\ 4/3\ \pi r^3$

$= b$

For n moles it is $nx4x\ 4/3\pi r^3$

$= nb$

We can remember it as:

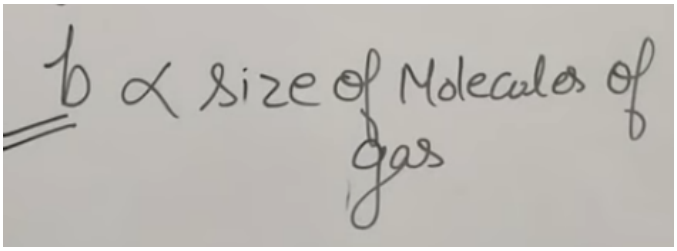
$$b = 4N_aV_r$$

Vr=Real volume.

Significance of b (vander waals constant for volume)

The vander Waals constant b is a measure of the size of the particles in a gas and their ability to interact with each other. In the vander Waals equation of state, b

represents the volume occupied by a mole of gas particles and their intermolecular interactions.



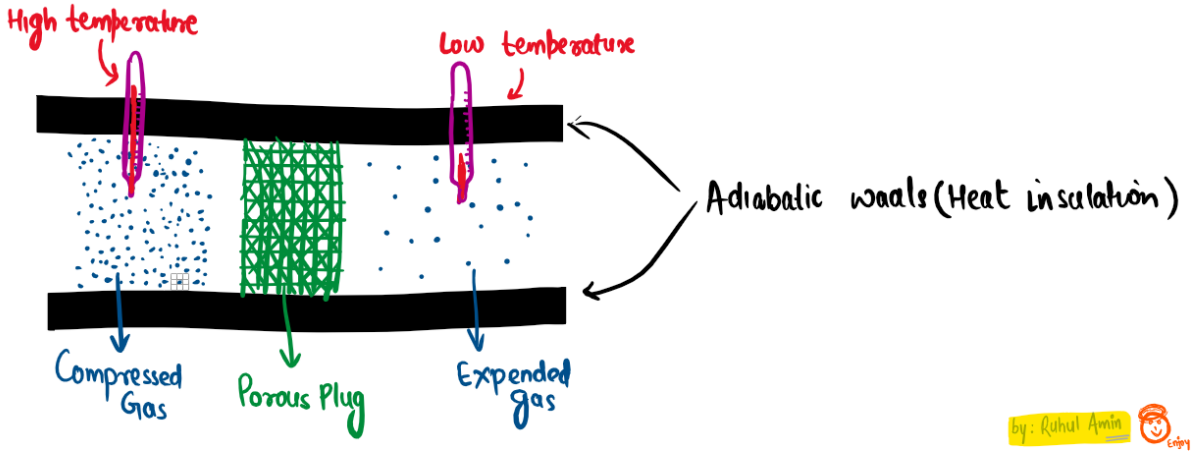
Evidence of Molecular Attration of gas:

• Gas molecules have vander waals force of attration,Otherwise gas could never be liquified or solidified.
• On liquification and solidification, we only tend to reduce kinetic energy (by lowing temperature) and reduce distance b/ w molecules (by high pressure).

> 💡 Molecular Attraction ultimately result in change in Pressure.

> Joule-Thomson effect is also the evidence.

Joule-Thomson effect

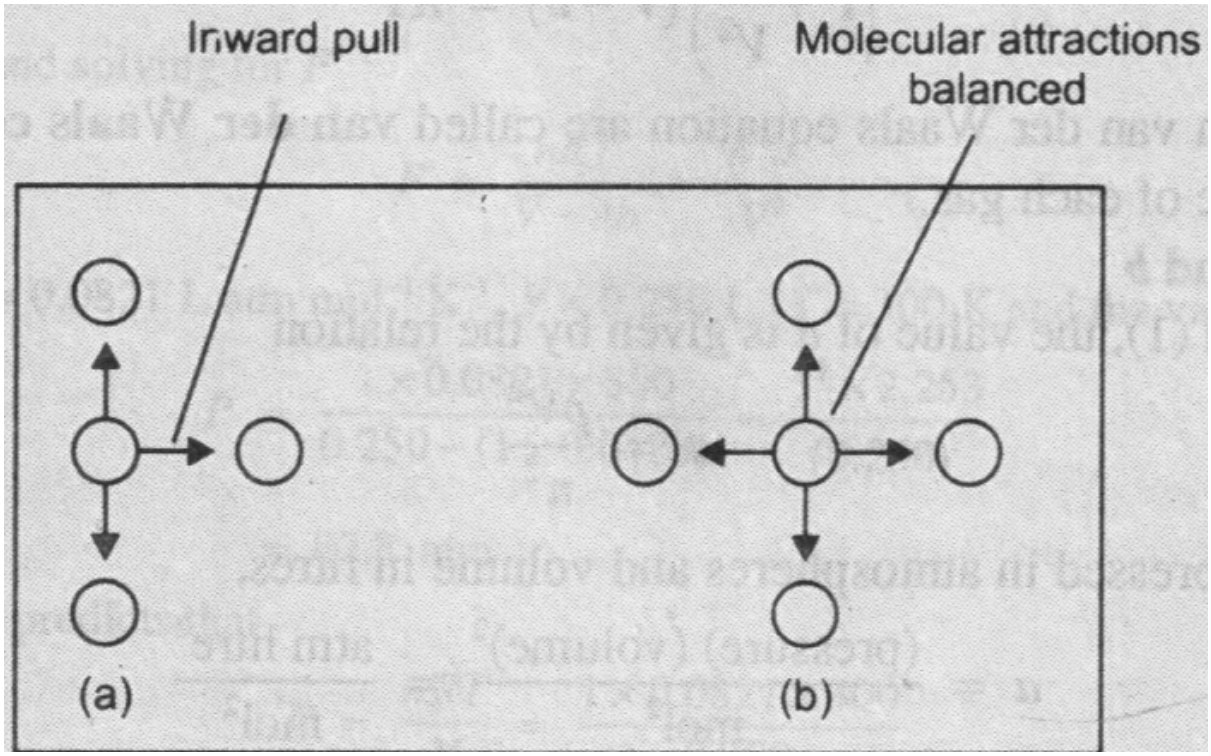


- When compressed gas is passed through porous plug in Adiabatic container the emerging gas is found to be cooler than entering gas

- This is because on expension, some work has to be done against the internal force of attraction, which require energy.
- This energy comes from the system itself.

Correction in pressure of Ideal gas for the real gas

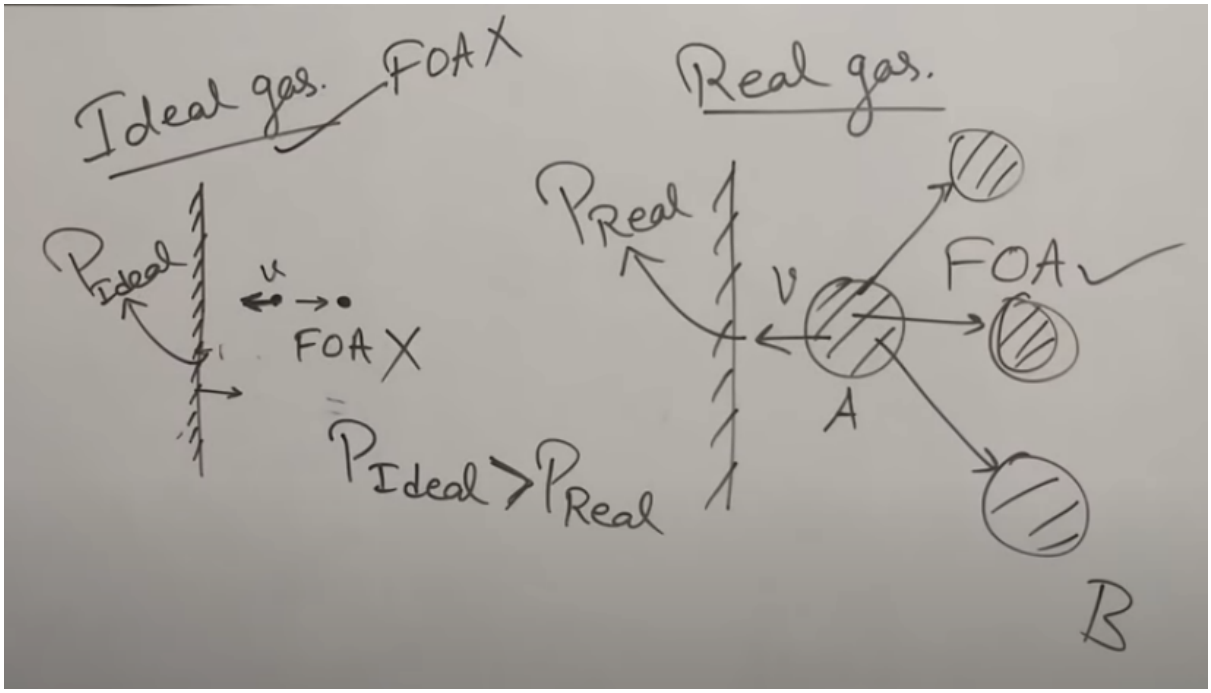
A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull (fig 2.8) due to unbalanced forces.



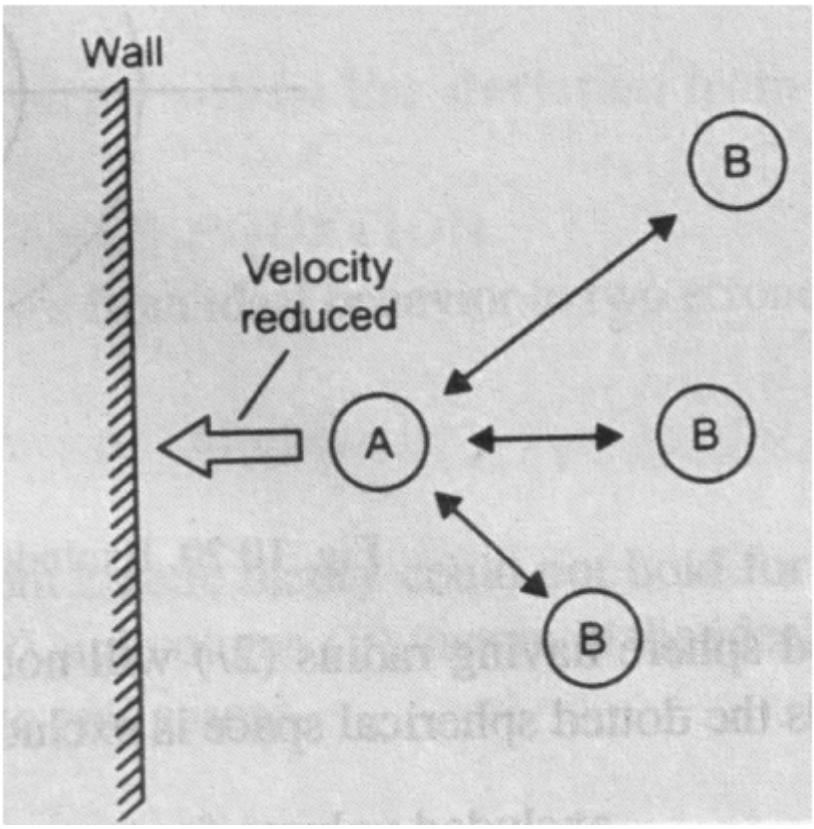
$$P = P_{ideal} - p$$

Or $$P_{ideal} = P + p$$

The value of p is determined by the force of attraction between molecules (A) stricking the wall of the container and molecules (B) pulling them inward (Fig 2.9).



Comparison between Ideal and real gas.



Real gas

For Ideal gas:

$$Pideal = Pexternal$$

For Real gas:

$$Pgas = Pexternal + Pinternal$$

The above equation is pressure correction.

The net force of attraction is, therefore, is proportional to the concentration of (A) type molecules and also of (B) type of molecules:

> 💡 The concentration of A type and B type is same because when goes to the place of B , it work as B and B goes to the place of A and work as A and visa-versa.

Concentration of A type of molecule= n/V

Concentration of B type of molecule= n/V

That is $p \propto C_A . C_B$

$p \propto A \frac{n}{V} \times \frac{n}{V}$

$p = an^2 / v^2$

Where,
C_A = Concentration of A
C_B = " " B
P = Pressure (internal)
V = Volume

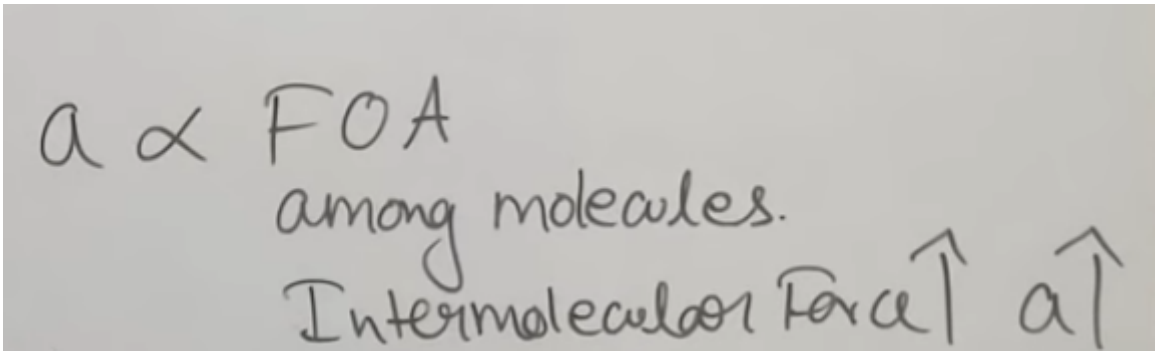
n = total number of gas molecules in volume V.

Hence pressure

$P_{gas} = P + an^2/V^2$

Significance of a (vander waals constant for pressure)

The vander Waals constant a is a measure of the strength of the intermolecular forces between the particles in a gas.



And FOA(Force of attraction) is vander waals force. It depends of Molar Mass.

> 💡 Value of a more ; Liquifiation more

Why value of a is zero for Hydrogen and helium?

- The value of the vander Waals constant a for hydrogen and helium is close to zero because these gases have very weak intermolecular forces. The vander Waals constant a is a measure of the strength of the intermolecular forces between the particles in a gas, and the weaker the intermolecular forces, the smaller the value of a.
- Hydrogen and helium have very low molecular weights and small sizes, which results in weak intermolecular forces between their particles. As a result, the vander Waals constant a for these gases is much smaller than for other gases with stronger intermolecular forces, such as nitrogen and oxygen.

Real Gas Equation or Van der Waals equation of state

- Van der Waals equation relates the relationship between the pressure, volume, temperature, and amount of Real gases.
- Furthermore more importantly, the Van der Waals equation is based on the molecular dimensions and molecular interactions with forces (attractive or repulsive forces).
- This is the modification of ideal gas law i.e **correction terms for pressure and volume** in ideal gas law.
- The equation is written as;

Expression for Van der Waals Equation for state :

Ideal Gas equation, $P_i V_i = nRT$

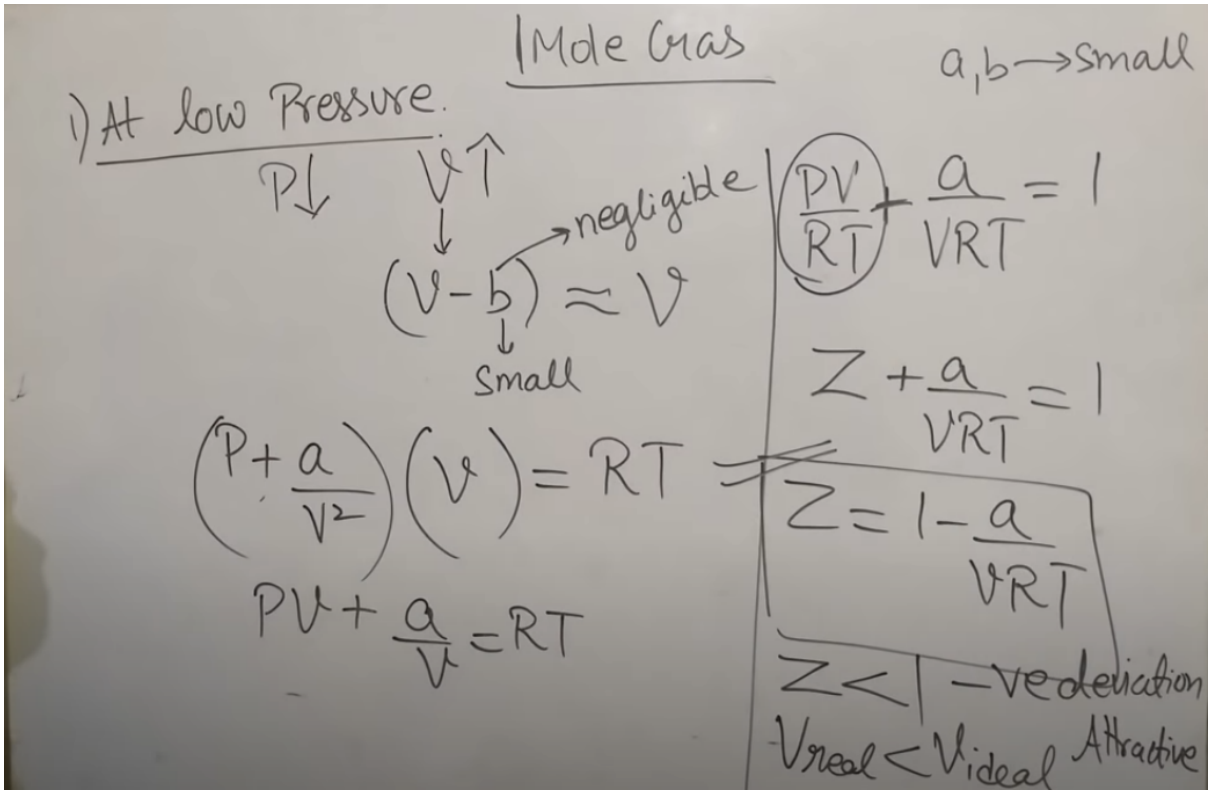
Real Gas equation, $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

- Real Gas equation is known as Van der Waals Equation.

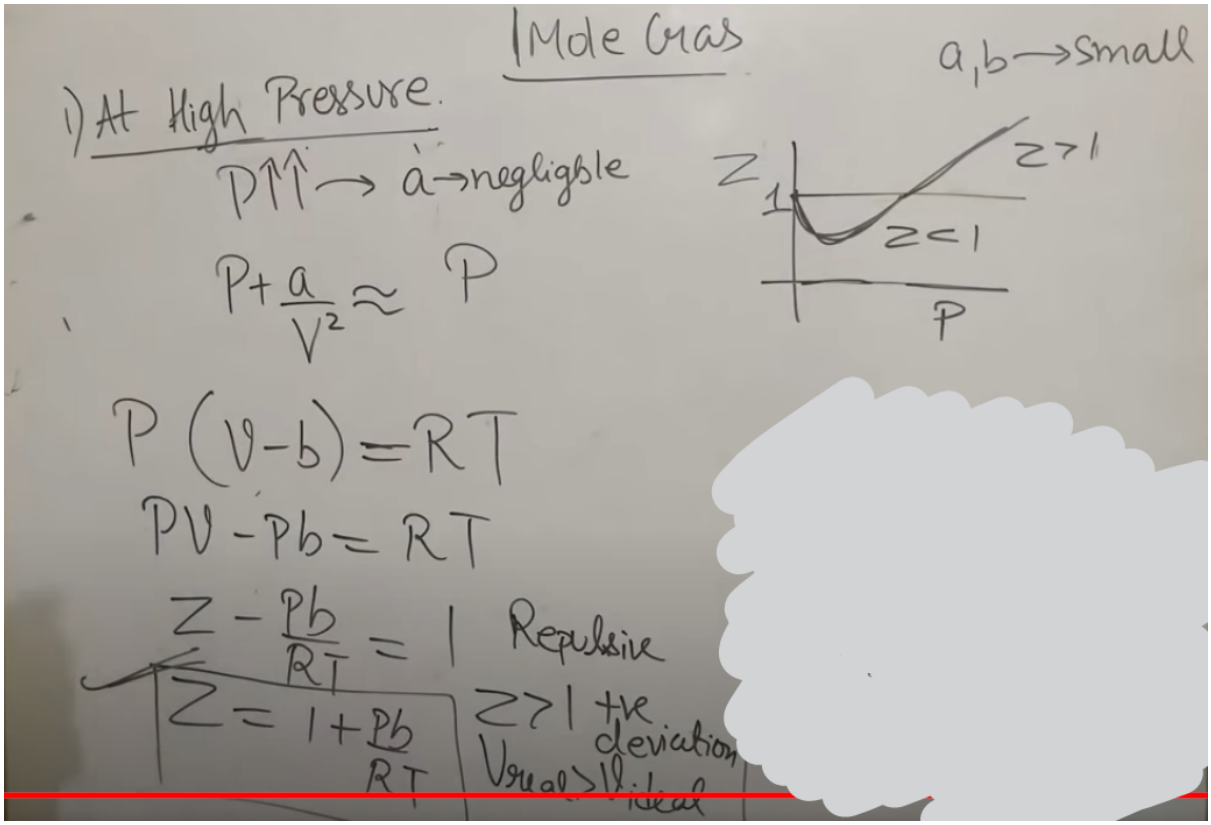
- The constants a and b have positive values and are characteristic of the individual gas.

Compressibility factor(Z) with respect to Real gas equation:

Low Pressure



High Pressure



High Temperature

Ideal Gas

Pressure zero

Ideal Gas

💡 LPHT forms ideal gas. i,e Low pressure and High Temperature